NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

APOLLO 16 MISSION

ANOMALY REPORT NO. 1

OXIDIZER DESERVICING TANK FAILURE

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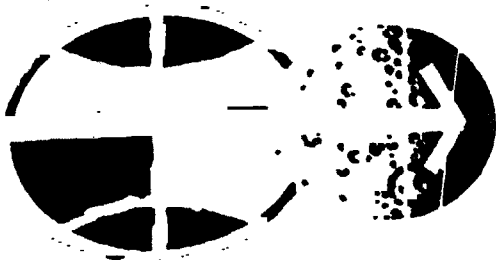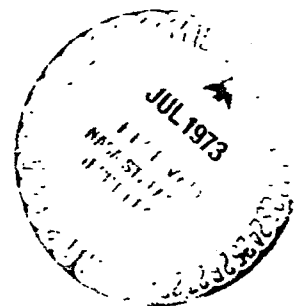
MANNED SPACECRAFT CENTER

HOUSTON, TEXAS

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CXIDIZER DESERVICING TANK FAILURE

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1.0 INTRODUCTION

An explosive failure of a ground support equipment decontamination
unit tank occurred during the postflight deactivation of the oxidizer (ni-
trogen tetroxide) portion of the Apollo 16 command module reaction control
system. A discussion of the significant aspects of the incident and con-
clusions are included in this report.

2.0 SUMMARY

The command module reaction control system is emptied of all remain-
ing propellant using ground support equipment designed to provide an acid/
base neutralization of the propellant in both the liquid and gaseous phases
so that it may be disposed of safely. During the deactivation operation of
the oxidizer from the Apollo 16 command module on May 7, 1972, the scrubber
tank of the decontamination unit exploded, destroying the ground support
equipment unit and damaging the building that housed the operation. Only
minor injuries were received by the personnel in the area and the command
module was not damaged.

Test results show that the failure was caused by an insufficient quan-
tity of neutralizer for the quantity of oxidizer. This insufficiency lead
to exothermic nitration-type reactions which produced large quantities of
gas at a very high rate and failed the decontamination tank.

3.0 GROUND SUPPORT EQUIPMENT

3.1 DESIGN CONSIDERATIONS

The ground support equipment oxidizer decontamination unit is a self-
contained unit for removing oxidizer and its vapors from the command module
reaction control system. This was to assure that the spacecraft would be
free of toxic vapors and would prevent degradation of spacecraft components.

The ground support equipment is designed for use in confined areas;
i.e.. on board ships, at the launch site, and at any port where the space-
craft may be off loaded from a recovery ship. Since adequate facilities
do not exist at these remote sites for disposal of toxic waste, provisions
were made to neutralize any oxidizer and oxidizer vapor removed from the
spacecraft and all liquids and gases required to inert the spacecraft were
contained within the unit.

The unit uses Delchem 2303C as a neutralizer for the oxidizer. Delchem 2303C, manufactured by Pennsalt Chemical Company, is composed of the following materials:

Triethanolamine (commercial grade)	70.0 percent by weight
Ethylene Glycol Monoethylether	10.0 percent by weight
Water	19.4 percent by weight
Wetting Agent	0.5 percent by weight
Anti-Foam Agent	0.1 percent by weight

The triethanolamine is a base and reacts with the acidic nitrogen tetroxide solution and forms nitrate salt. In aqueous solution, the nitrogen tetroxide exists as a equimolar mixture of nitric acid (HNO_3) and nitrous acid (HNO_2). The neutralization reaction between triethanolamine and nitrogen tetroxide in aqueous solution is:

$$2(HOCH_2CH_2)_3N + N_2O_4 + H_2O \longrightarrow (HOCH_2CH_2)_3N \cdot HNO_3$$

$$+ \quad (HOCH_2CH_2)_3N \cdot HNO_2$$
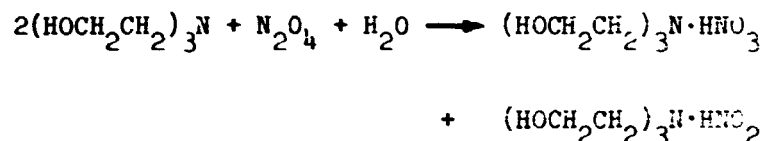
Based on this reaction, one pound of nitrogen tetroxide requires a minimum of 4.63 pounds of Delchem 2303C to achieve neutralization, or volumetrically, one gallon of nitrogen tetroxide requires 6.1 gallons of Delchem 2303C.

3.2 NORMAL DECONTAMINATION PROCEDURES

Figure 3-1 shows a simplified schematic of the decontamination unit which consists of a gaseous nitrogen supply stored in K-bottles, a Freon storage tank, a collector tank to receive oxidizer from the spacecraft, and a scrubber tank which contains the neutralizer. The unit also has numerous valves, regulators, and connectors which interface with the spacecraft. The basic procedures for removing the oxidizer and oxidizer vapor from the spacecraft are as follows:

a. Connect the ground support equipment lines to the spacecraft as shown in figure 3-1 at the ground support/reaction control system interface.
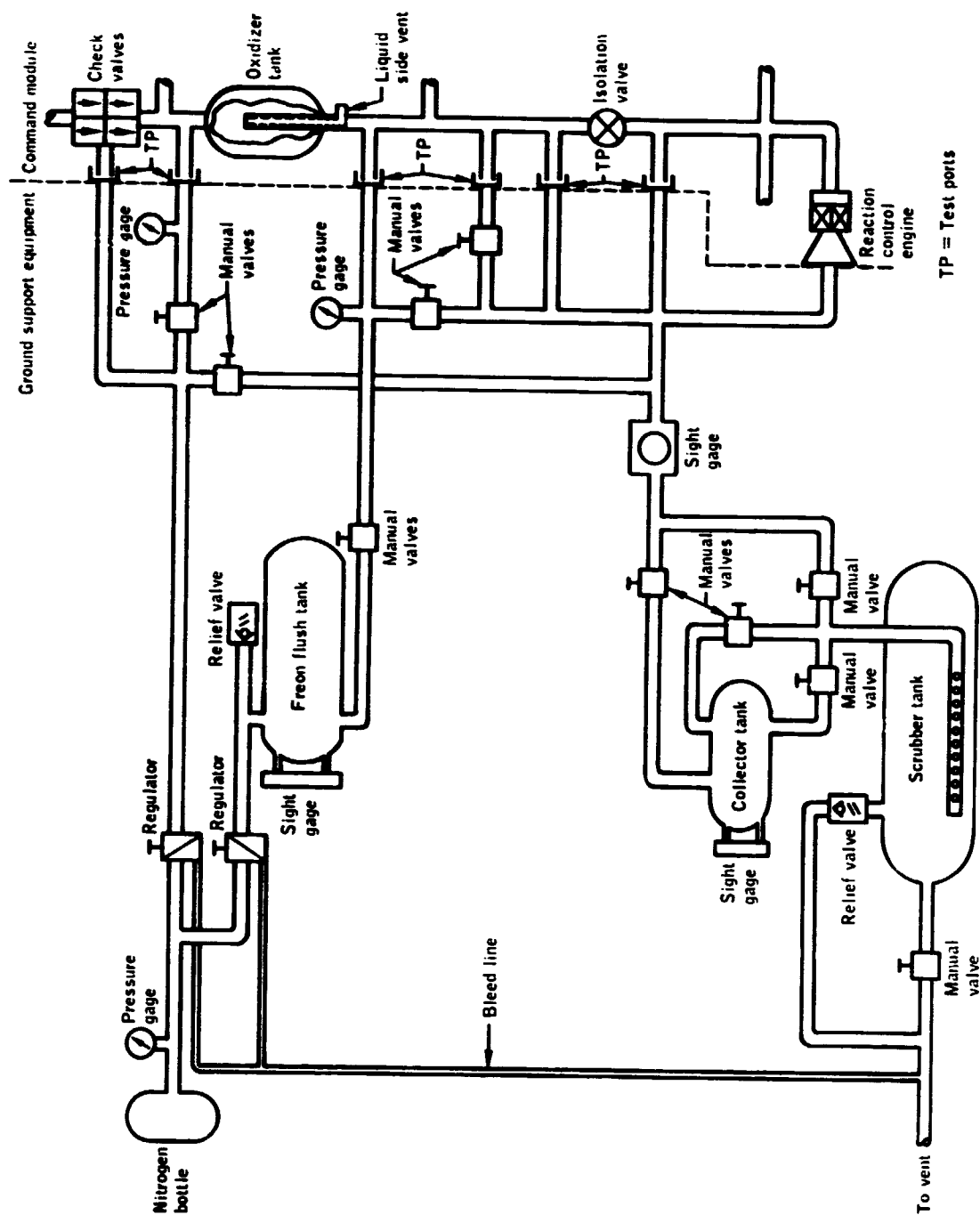
Figure 3-1.- Simplified schematic of reaction control system decontamination unit.

b. Apply low-pressure gaseous nitrogen to the gas side of the space-
craft propellant tank bladders forcing the liquid oxidizer from the space-
craft tanks into the collector tank.

c. Purge with gaseous nitrogen through the spacecraft liquid-side
vent with the gaseous nitrogen returning to the collector tank in sequence
from each of the connections downstream of the spacecraft propellant tanks.
The gaseous nitrogen and any oxidizer vapor would then flow from the col-
lector tank into the scrubber tank and finally out through the scrubber
tank vent.

d. The oxidizer is then drained from the collector tank into the
scrubber tank to be neutralized.

e. The oxidizer tank and spacecraft plumbing downstream of the tank
is then filled with Freon. After allowing several minutes for the oxidi-
zer to mix with the Freon, the fluid is forced from the spacecraft direct-
ly into the scrubber tank. During this period, low-pressure gaseous ni-
trogen is applied to the Freon flush tank forcing Freon from this tank
through the liquid side vent in the spacecraft propellant tank and out the
various spacecraft connections downstream of the spacecraft oxidizer tank
and into the ground support equipment scrubber tank.

f. The Freon is then removed from the spacecraft by purging with low-
pressure gaseous nitrogen through the liquid-side vent and out through the
numerous spacecraft-to-ground support equipment connections. The gaseous
nitrogen is bubbled through the scrubber tank fluid and vented.

4.0 EVENTS ATTENDING FAILURE

The ground support equipment was serviced in accordance with the de-
activation procedure as follows:

Flush Tank - 150 gallons of Freon (tank capacity - 150 gallons)

Collector Tank - 2 gallons of water (tank capacity - 10 gallons)

Scrubber Tank - 10 gallons of neutralizer, 30 gallons of water
              (tank capacity - 205 gallons)

Table 4-I shows the pertinent sequence of events. The operation was
normal through item 4 (Table 4-1) where the draining of the collector tank
was a deviation to the procedure required to provide space for the quan-
tity of oxidizer remaining in the spacecraft. During this draining pro-
cess, the scrubber tank became very warm, bubbling sounds were heard, and

TABLE 4-I.- PERTINENT TIMELINE FOR APOLLO 16 OXIDIZER DEACTIVATION.

May 7, 1972					
5:00	6:00	7:00	8:00	9:00	10:00

Time, a.m., P.d.t.

(1) △ Start oxidizer drain

(2) △ Collector tank full

(3) △ Fumes from scrubber tank vent

(4) △▭ 3.5 gallons drained from collector tank into scrubber tank

(5) △▭ Gaseous nitrogen purge dump into collector tank

(6) Ice formed on △▭ collector tank

(7) △▭ Collector tank drained into scrubber tank

(8) Reaction control system filled with Freon △▭ for soak

(9) Reaction control system Freon flush △

(10) Pressures rapidly increasing and explosion △

the venting of oxidizer fumes increased. The expulsion of the remaining oxidizer in the reaction control system into the collector tank was completed after which the system was purged with nitrogen.

The tank icing noted in item 6 (Table 4-I) resulted from expansion cooling of the purge gas and evaporation of the oxidizer. During the draining of the oxidizer from the collector tank into the scrubber tank, heating and a rumbling noise within the scrubber tank occurred. The oxidizer system was filled with Freon and allowed to soak for 30 minutes. When the Freon was expelled into the scrubber tank, violent bubbling noises were heard coming from the tank. The whole decontamination unit began shaking, and the pressure gages of the flush and scrubber tanks fluctuated and increased. The scrubber-tank vent hose came out of the barrel and whipped around. The scrubber tank then ruptured.

5.0 DECONTAMINATION UNIT DESIGN LIMITATIONS

5.1 GASEOUS NITROGEN SYSTEM RELIEF CAPABILITY

Two regulators are used in the decontamination unit to reduce the gaseous nitrogen pressure stored in K-bottles (fig. 5-1). One regulator supplies gaseous nitrogen directly to the spacecraft for purge operations, and the other pressurizes the Freon flush tank. The systems downstream of both regulators are protected by a 47-psi relief valve which, in the full open position, has an area equivalent to a 0.049 square-inch orifice. Calculations indicate that a regulator failing in the full open position would produce a maximum system pressure of 130 psi. This exceeds the 60 psi proof pressure for the system but is less than the calculated 338 psi burst pressure of the scrubber tank.

5.2 SCRUBBER TANK RELIEF CAPACITY

The scrubber tank was designed to be protected from overpressurization by a relief valve installed in parallel with the scrubber tank vent valve as shown in figure 5-1. The vent valve, relief valve, and reference or ambient sensing side of the two gaseous nitrogen regulators were all connected to a vent line about 120 feet in length. This effectively placed a small orifice in series with the parallel vent/relief system. The relief system on the scrubber tank was not capable of venting the high rate of gasing during the exothermic nitration-type reactions which occurred during detanking operations. Apparently, the relief valve was intended
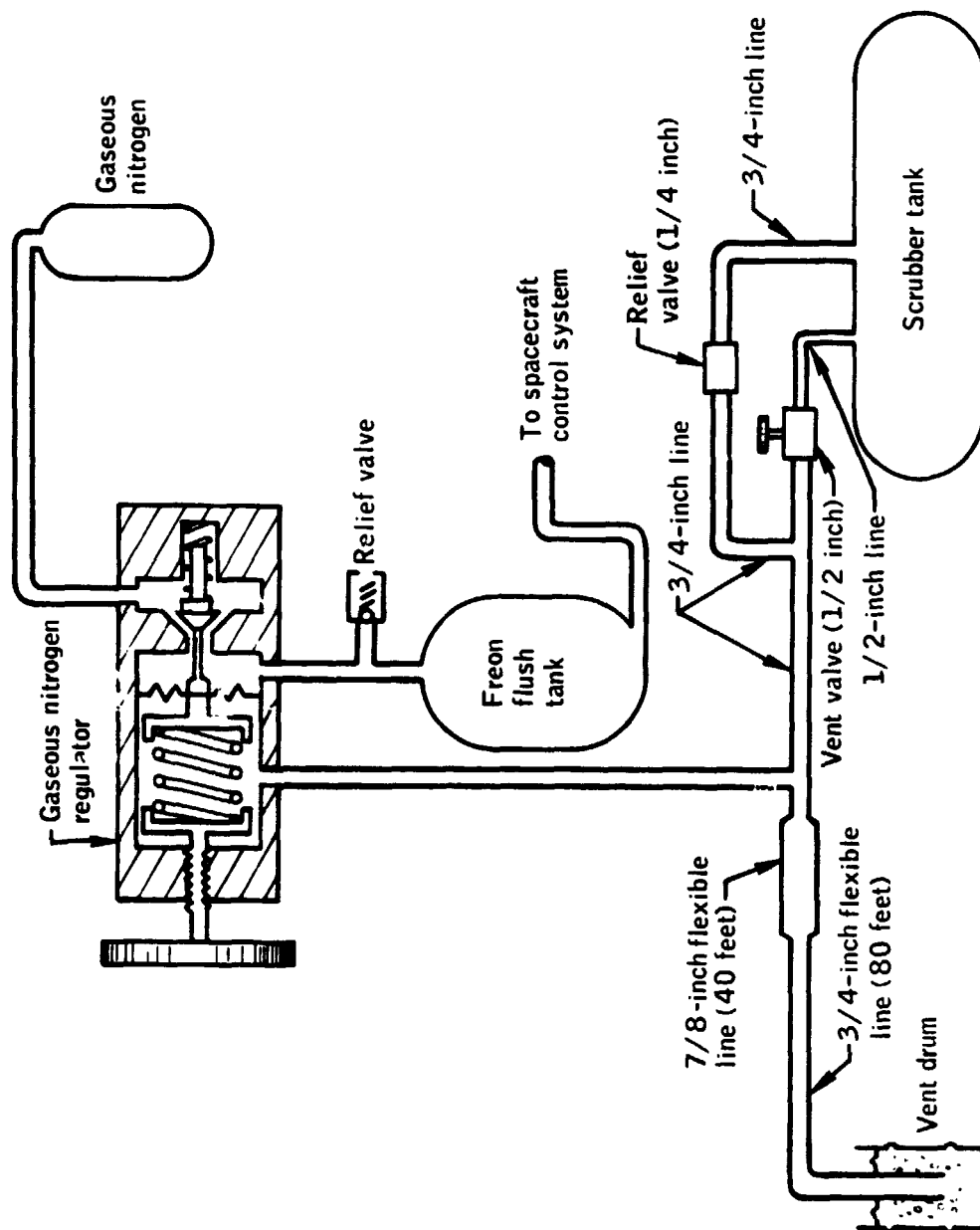
Figure 5-1. - Scrubber tank vent/relief system.

to prevent a pressure buildup in the scrubber tank during filling or purging operations if the vent valve was inadvertently left closed.

Plumbing of the relief valve discharge and the reference side of the regulators into the main vent line is poor design practice. The vent line could be plugged as easily as the vent valve left closed. This would not only prevent the relief valve from relieving, but also would drive the regulator wide open.

Since the entire vent system was designed to handle only the gaseous nitrogen from the purge operations, it did not have the capacity required to handle the large quantities of gas produced by the type of chemical reaction which was present.

5.3 SCRUBBER TANK STRUCTURAL CAPABILITY

An examination of the tank indicated that a ductile failure occurred in the heat-affected zone of the longitudinal weld. The tank burst pressure capability as a function of temperature is shown in figure 5-2. The burst pressure is based on a weld allowable of 24 000 psi. The measured strength in the typical weld section was 25 000 psi.

Tank material samples were examined for degradation due to corrosion. The maximum corrosion observed would decrease tank strength by no more than 25 percent. The reduced burst pressure due to corrosion is also shown in figure 5-2. Note, however, that continued use of this tank in decontamination operations would have ultimately resulted in corrosion-induced leakage.

The energy released by the tank explosion based on a 338-psi burst pressure is equivalent to a minimum of 1.75 pounds of trinitrotoluene (TNT). However, based on the damage to the building, estimates of trinitrotoluene equivalent are as high as 10 pounds.

6.0 CHEMICAL TESTS

A chemical test program was initiated at the Manned Spacecraft Center to determine the chemical composition of the Delchem 2303C neutralizer; to determine pertinent physical, chemical, and thermodynamic properties of the neutralizer; and qualitatively and quantitatively to characterize the chemical reactions which occur between nitrogen tetroxide and the constituents of the Delchem 2303C.
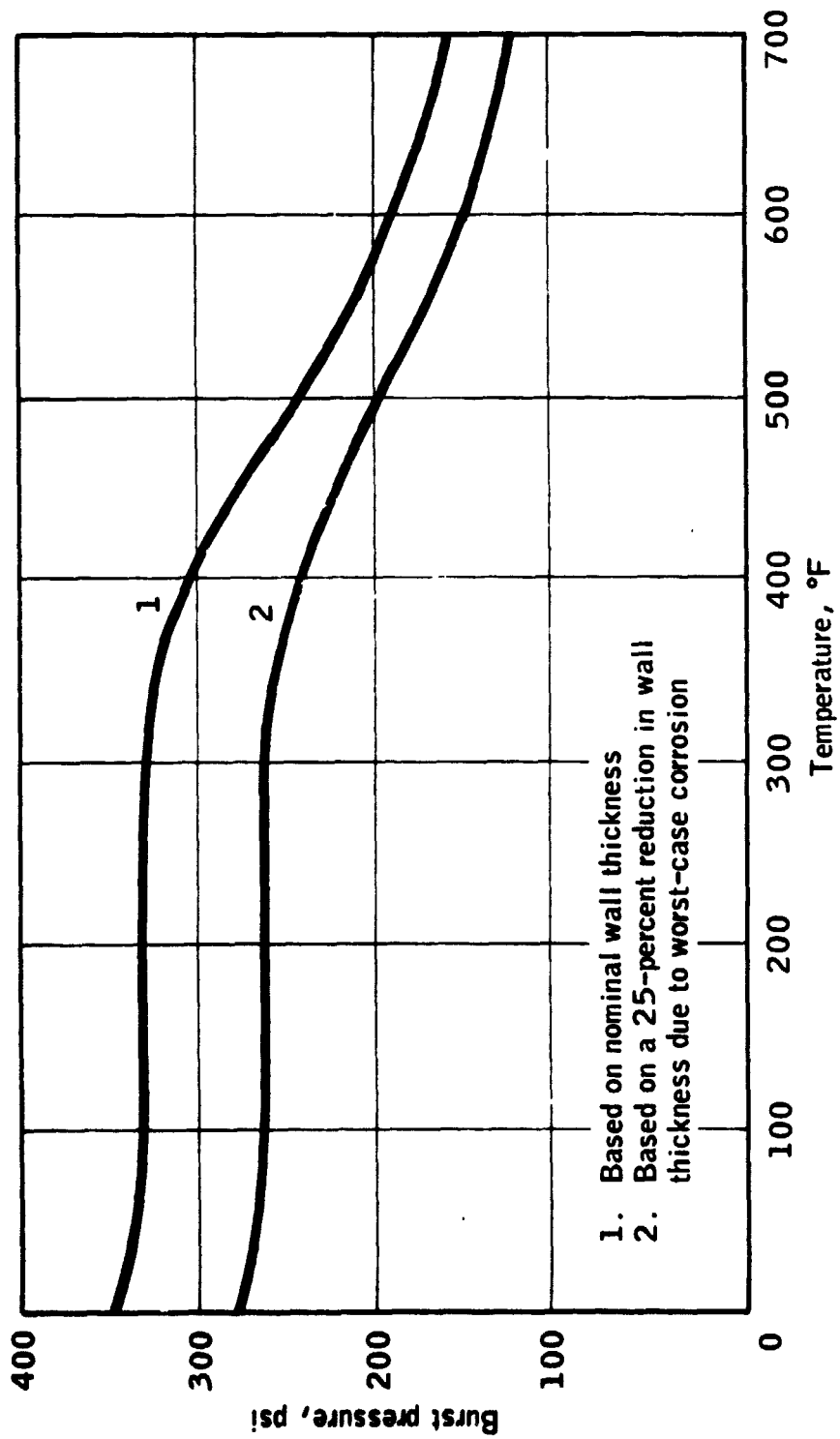
Figure 5-2.— Scrubber tank burst pressure as a function of temperature.

1. Based on nominal wall thickness
2. Based on a 25-percent reduction in wall thickness due to worst-case corrosion

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All tests in this effort were performed with small quantities of reactants in laboratory glassware either in an open system or in a confined system under very low gage pressures. Although the solution concentrations and relative quantities of reactants used, in general, simulated those of the failure, no attempt was made to simulate other variables such as the timeline, solution temperature and pressure, reactant addition rate and dispersal method, solution geometry, surface-to-volume ratio, and rate of heat loss to the surroundings.

The Delchem 2303C used in the.. tests was from the same lot used during the Apollo 16 decontamination. A chemical assay of the Delchem 2303C was performed, and these data are presented in tables 6-I and 6-II.

Several tests were made to characterize the reactions which occur between nitrogen tetroxide and the constituents of Delchem 2303C. These tests can be categorized as follows:

    a. Effect of the quantity of Delchem 2303C when it is equal to, or in excess of, that quantity required to neutralize the nitrogen tetroxide.

    b. Effect of the quantity of Delchem 2303C when it is insufficient to neutralize the nitrogen tetroxide.

    c. Special tests investigating alternate neutralization techniques or the effect of other variables.

A detailed discussion of the tests, including data plots, is included in the Appendix of this report.

Tests 1 and 2, summarized in table 6-III, show the effects when sufficient or excess Delchem is present to neutralize the oxidizer. A heat release was observed in these two tests upon the addition of the nitrogen tetroxide/water solution to the Delchem 2303C/water solution, and this is in. cative of an acid-base type neutralization. The neutralization reaction is rapid – essentially instantaneous – and no gas is evolved as a result of the neutralization reaction. No secondary or additional reactions were observed to occur after the neutralization reaction. The addition of a small quantity of 95-percent Freon TF/5-percent nitrogen tetroxide (by volume), simulating events during the tank failure, had no effect and promoted no additional or secondary reactions.

In addition, two tests were performed to measure the heat of neutralization of Delchem 2303C and nitrogen tetroxide. These tests were performed in an open, vacuum-jacketed flask and involved the rapid mixing of nitrogen tetroxide/water solutions with Delchem 2303C/water solutions. In both cases, a slight excess of Delchem 2303C was used. After the initial exothermic neutralization reaction occurred, the solu'.ons were allowed to stand for several hours of observation. Again, no evidence of any additional reaction was observed.

TABLE 6-I.- CHEMICAL ASSAY OF DELCHEM 2303C USED IN
COMMAND MODULE REACTION CONTROL SYSTEM DECONTAMINATION

Component	Nominal Specification Requirements, percent	Measured, percent
Triethanolamine	70.0	70.4
Water	19.4	22.1
Ethylene Glycol Mono-ethylether[1]	10.0	4.6
Additives	0.6	-

[1]Ether concentration determined by difference after total
alkalinity and water were determined. Additive concentra-
tion was not determined.

Note: Total alkalinity of 73.3 includes ethanolamine, diethano-
lamine, and triethanolamine. The mono- and di- amines are impurities in
the triethanolamine.

TABLE 6-II.- PERTINENT PROPERTIES OF DELCHEM 2303C

Parameter	Value
Density (25°C)	1.0955 gm/ml
Heat capacity (25°C)	0.495 cal/gm-°C
pH	10.85
Heat of solution in water	8.1 calories per gram of Delchem 2303C
Heat of reaction with nitrogen tetroxide.	16 400 calories per gram-mole nitrogen tetroxide neutralized
Boiling point of 25-percent Delchem 2303C/75-percent water (by volume) at one atmosphere	99.5°C

TABLE 5-III.- SUMMARY OF TESTS

Test No.	Delchem 2303C/water solution		Nitrogen tetroxide/water solution				Reaction system[1]	Results and observations[2]
	Concentration[3]	Volume	Concentration[3]	Volume	Method of addition	Rate of addition		
EFFECTS OF TESTS WITH SUFFICIENT OR EXCESS DELCHEM 2303C FOR NITROGEN TETROXIDE NEUTRALIZATION								
1	25 percent Delchem, 75 percent water	360 ml	85 percent nitrogen tetroxide, 15 percent water	3 ml	Via burette under the surface	4.5 minutes	Open beaker	Temperature increased from 23° C to 25° C. No secondary reactions observed. Subsequent addition of 2 ml of 95 percent Freon TF/5 percent nitrogen tetroxide had no effect. Quantity of Delchem 2303C used is 6 times in excess of that required to neutralize the nitrogen tetroxide.
2	25 percent Delchem, 75 percent water	120 ml	85 percent nitrogen tetroxide, 15 percent water	6 ml	Via burette under the surface	5 minutes	Open beaker	Quantity of Delchem 2303C used is that necessary to provide exact neutralization of nitrogen tetroxide. Temperature increased from 22.5° C to 34.8° C. No secondary reactions observed. Subsequent addition of Freon TF/nitrogen tetroxide had no effect.
EFFECTS OF TESTS WITH EXCESS NITROGEN TETROXIDE								
3	25 percent Delchem, 75 percent water	20 ml	85 percent nitrogen tetroxide, 15 percent water	6 ml	Via burette under the surface of solution	4 minutes	Open beaker	Simulates Apollo 16 incident in solution concentrations and relative quantities. Temperature increased from 22.2° C to 40° C and then cooled to room temperature. No secondary reaction observed. No effect of Freon TF/nitrogen tetroxide addition observed.
4	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under the surface of solution	2 minutes	Open vacuum jacketed flask (400 ml)	Simulates Apollo 16 incident. Initial Delchem solution temperature 9.5° C. Temperature 34° C after 88 minutes. Addition of extra 4 ml of nitrogen tetroxide/water solution produced vigorous secondary reaction with 98° C peak temperature.
5	31 percent Delchem, 69 percent water	32 ml	50 percent nitrogen tetroxide, 50 percent water	20 ml	Via burette under the surface of solution	6 minutes	Open vacuum jacketed flask (400 ml)	Simulates Apollo 16 incident (see Appendix for rationale). Immediate secondary reaction noted with vigorous gas evolution, reaching 101° C after 18 minutes.

TABLE 5-III.- SUMMARY OF TESTS (CONTINUED)

Test No.	Delchem 2303C/water solution Concentration[3]	Volume	Nitrogen tetroxide/water solution Concentration[3]	Volume	Method of addition	Rate of addition	Reaction system[1]	Results and observations[2]
6	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	2.5 minutes	Open vacuum Jacketed flask (400 ml)	Simulates Apollo 16 incident. Got slowly accelerating secondary reaction reaching peak temperature of 87° C after 40 minutes.
9	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	12 minutes	Closed system. Distillation flask reactor and 5-gallon gas receiver flask.	Simulates Apollo 16 incident. Gage pressure 1 to 2 inches water. Temperature 1 eased from 21.8° C to 41.0° C. No runaway secondary reaction occurred. System leaked - no gas displacement measured.
10	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	10 minutes	Same as 9, but with 400 ml vacuum jacket vacuum flask as reactor.	Simulates Apollo 16 incident. No runaway secondary reaction occurred. Peak temperature 47.2° C after 99 minutes. Addition of extra nitrogen tetroxide/water solution did not promote runaway reaction. Volume of gas evolved was 3665 ml.
11	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	5.5 minutes	Same as 9, but with 400 ml vacuum jacket flask as reactor.	Simulates Apollo 16 incident. No runaway secondary reaction occurred. Initial Delchem 2303C/water temperature equaled 33.5° C. Peak temperature equaled 54.0°C after 50 minutes. Addition of extra nitrogen tetroxide/water was ineffective. Gas volume evolved was 2350 ml.
12	25 percent Delchem, 75 percent water	40 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	7 minutes	Closed system. Distillation flask reactor and 5-gallon gas receiver flask.	Simulates Apollo 16 incident. Runaway secondary reaction occurred. Initial temperature 28.5° C. Peak temperature 96.5° C after 42.5 minutes. Gas volume evolved was 4770 ml.

TABLE 5-III.- SUMMARY OF TESTS (CONCLUDED)

Test No.	Delchem 1030/water solution		Nitrogen tetroxide/water solution				Reaction system[1]	Results and observations[2]
	Concentration[3]	Vol.	Concentration[3]	Volume	Method of addition	Rate of addition		
SPECIAL TESTS								
7	16.7 percent Delchem, 83.3 percent water	60 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	5.5 minutes	Open vacuum jacketed flask (400 ml)	To investigate effect of additional inert thermal mass on secondary reaction. Initial temperature 23.5° C. Peak temperature 38.5° C. No runaway secondary reaction.
8	2 Normal sodium hydroxide solution	200 ml	85 percent nitrogen tetroxide, 15 percent water	12 ml	Via burette under surface of solution	15 minutes	Open vacuum jacketed flask (400 ml)	To demonstrate alternate method of nitrogen tetroxide neutralization. Initial temperature 27.5° C. Peak temperature 42.8°C. Quantity of sodium hydroxide is 25 percent excess over amount needed. No gas evolved. No secondary reactions.

[1] All concentrations were measured by volume.

[2] Much nitrogen tetroxide vapor lost from reaction flask due to high volatility.

[3] See Appendix for additional data.

Tests 3 through 6 and 9 through 12, summarized in table 6-III, show the effects when insufficient Delchem is present to neutralize the oxidizer. Tests 3 through 6, carried out in open glassware systems, demonstrated the occurrence of a vigorous, exothermic, gas-evolving secondary reaction which takes place after the initial neutralization reaction has occurred. These tests also indicated that test parameters such as initial solution temperatures, quantity of excess nitrogen tetroxide, and rate of energy loss from the reaction system to the surroundings are also important to the occurrence of this secondary reaction. Tests 9 through 12, carried out in closed systems under gage pressures of 1 to 2 inches of water, demonstrated the unpredictability and non-repeatability of the secondary reaction. These tests also resulted in a rough measurement of the quantity and identity of the gas evolved from the secondary reaction.

Tests 7 and 8, summarized in table 6-III, show the effects of other variables. Test 7 investigated the secondary reaction occurrence with a simulated 16.7-percent Delchem 2303C/83.3-percent water solution (i.e.. 10 parts Delchem 2303C to 50 parts water by volume) rather than the 25-percent Delchem 2303C/75-percent water solution which was used in the failure case. With the additional inert thermal mass in the system, the runaway secondary reaction did not occur. No conclusions can be drawn from this, however, due to the apparent unpredictability of the secondary reaction. Test 8 investigated the use of a dilute (2 Normal) sodium hydroxide solution to neutralize the nitrogen tetroxide. In this case, a normal acid-base neutralization reaction was observed to occur instantaneously, without gas evolution, and without any additional or secondary reactions occurring.

Based on the results of these tests, under the conditions in which they were performed, the following conclusions can be drawn:

1. When sufficient Delchem 2303C is available to neutralize the nitrogen tetroxide present, no secondary exothermic, gas-evolving reactions occur.

2. When insufficient Delchem 2303C is available to neutralize the nitrogen tetroxide, and the nitrogen tetroxide is present in great excess (i.e., 5 to 6 times the amount which could be neutralized), a vigorous, exothermic, gas-evolving secondary reaction can occur.

3. The solution temperatures, quantity of excess nitrogen tetroxide, and rate of heat loss from the reacting system to the surroundings are important in determining whether the secondary reaction will accelerate and "run away".

4. The secondary reaction occurrence does not appear to be repeatable or predictable.

5. The introduction of Freon TF or the presence of metallic surfaces (such as the aluminum tank) is not necessary to the occurrence of the secondary reaction.

6. Because of the high volatility of the nitrogen tetroxide/water solution, layering of the nitrogen tetroxide/water in the Delchem 2303C/ water solution is unlikely. The nitrogen tetroxide/water solution boils as it is introduced into the Delchem 2303C/water solution and the bubbles of nitrogen tetroxide vapors provide much agitation to the solutions, preventing any layering. When Delchem 2303C is poured into water without subsequent agitation, layers are formed with the heavier Delchem 2303C below the water.

7.0 CAUSE OF FAILURE

A literature evaluation was made of the chemical processes which may have caused the failure of the scrubber tank. The following major reaction possibilities were considered from the components available at the time of failure:

a. Reaction of nitrogen tetroxide with the Freon TF

b. Reaction of Freon TF with the aluminum tank

c. Reactions of nitrogen tetroxide with triethanolamine beyond neutralization

d. Reactions of nitrogen tetroxide with ethylene glycol monoethylether.

Possibilities a and b were found unlikely for the conditions that existed and therefore, probably did not contribute to the failure. Reactions c and d appear to be the most likely processes which could have caused the failure and are discussed in the following paragraphs.

The products of the following reaction are soluble in water and stable if the reaction is stopped at this point.

$$2(CH_2CH_2OH)_3N + N_2O_4 + H_2O \longrightarrow (CH_2CH_2OH)_3NHNO_3 + (CH_2CH_2OH)_3NHNO_2$$
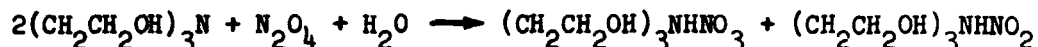
If, however, there is an excess of nitrogen tetroxide, as was the case, nitration of the reaction products may occur as follows:

$$(CH_2CH_2OH)_3NHNO_3 + N_2O_4 + H_2O \longrightarrow (CH_2CH_2-ONO_2)_3NHNO_3$$
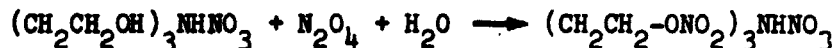
These reaction products, specifically triethanolamine tetranitrate, are unstable especially in excess acid (nitrogen tetroxide and water) and at slightly elevated temperatures. Several of these compounds, the decomposition of which produce large amounts of heat and gaseous products at unpredictable rates, are listed in reference 1. The nitration of the other major component of the neutralizer (ethylene glycol monoethylether) leads to reaction products of the same family as the triethanolamine reaction products. Although these products are not specifically listed in reference 1, they are unstable and also contributed to the failure.

In summary, the reactions of Delchem 2303C with excess nitrogen tetroxide at slightly elevated temperatures caused the observed failure. The other components (Freon TF and aluminum) of the system were not significant, except for stirring effects, in contributing to the failure.

8.0 HISTORY OF USE OF DELCHEM 2303C

The neutralizer solutions, known as Delchem, were developed for use in cleaning and decontaminating rocket engines using nitrogen tetroxide and Aerozine 50 propellants. As such, they were used to dissolve all propellant residues left in the engine hardware after multiple flushings with water. These solutions were used on the Titan II program to decontaminate the flight engines after ground testing and on the Gemini spacecraft during post-recovery deactivation.

The following incidents occurred during the use of the neutralizers:

a. During testing on October 17, 1965, on Launch Complex 19 of the Eastern Test Range, approximately 2 1/2 gallons of nitrogen tetroxide were drained into a 55-gallon drum containing a mixture of 10 quarts of water and one quart of triethanolamine. The drum exploded while being moved away from Launch Complex 19 by a forklift truck.

b. A report published by the Kennedy Space Center Safety Office on April 22, 1966, entitled "Report of Inquiry on Launch Complex 34 Nitrogen Tetroxide Drum Explosion," no report number, indicated that a drum (55-gallon) exploded after nitrogen tetroxide was placed into it. The explosion occurred while the drum was being transported to a disposal area. The report indicated that there might have been some other fluid in the drum, such as a Freon.

As a result of the two incidents and information available as of August 1966, the use of Delchem 2303C to "neutralize" nitrogen tetroxide should have been discontinued until sufficient testing was performed to

define the proper quantity of Delchem 2303C per unit weight of nitrogen tetroxide, the proper ratio of water to Delchem 2303C, and the necessary conditions and procedures to use safely the Delchem 2303C.

9.0 CONCLUSIONS

The following conclusions are made as a result of this investigation:

1. The explosion that destroyed the decontamination unit (SN-001) during deactivation of the Apollo 16 spacecraft at San Diego was caused from rapid overpressurization of the scrubber tank.

2. The quantity of Delchem which was used in the scrubber tank was insufficient to neutralize the large quantity of oxidizer. The decontamination unit contained less than one gallon of Delchem for each gallon of oxidizer. A ratio of 6 to 1 by volume is required to neutralize the oxidizer.

3. Exothermic reactions involving decomposi .on of nitration-type components occurred between the excessive nitrogen tetroxide (oxidizer) and the constituents of the neutralizer and produced gases at a rate which exceeded the capacity of the scrubber tank vent system.

10.0 CORRECTIVE ACTIONS

The Apollo 16 Deactivation Incident Investigation Board recommended that certain corrective actions be implemented for postflight deactivation and decontamination of the reaction control system on the Apollo 17 command module and all subsequent Apollo command modules. These corrective actions were approved by the Apollo Spacecraft Program Office Configuration Control Board contingent upon a successful demonstration of the deactivation/decontamination operation using the actual equipment and procedures called for in the recommendations and the personnel assigned to conduct the mission operations. The demonstration showed that all elements of the operation were satisfactory; therefore, the corrective measures will be instituted. They are summarized as follows.

1. The requirement to neutralize residual propellants at the deactivation site was eliminated and changes were made in the deactivation procedures and equipment. The following procedural changes will be effected:

(a) The oxidizer and fuel will be expelled from the spacecraft and deposited separately into special transportable containers that have been approved by the Department of Transportation.

(b) The system will be flushed with freon for the oxidizer side and with alcohol for the fuel side and the contaminated flush fluids will be collected separately in containers that have been approved by the Department of Transportation.

(c) Both portions of the system will be purged separately with heated nitrogen until dry.

(d) For landings in the Pacific Ocean, the residual propellants and the contaminated flush fluids will be transported to the White Sands Test Facility for final disposal according to prescribed procedures. For Atlantic Ocean landings, the residual propellants and contaminated flush fluids will be disposed of at the Kennedy Space Center.

2. Control of all procedures and paperwork related to postflight deactivation and decontamination activities was formalized to insure that all appropriate organizational elements are included in change/approval cycles.

3. A Deactivation/Decontamination Manager was appointed. He reports directly to the responsible MSC Program Manager, and his function is to oversee all activities related to postflight deactivation and decontamination of the command module reaction control system. His efforts will be supported by personnel assigned from the Safety Office, the Reliability and Quality Assurance Divisions, the Flight Operations Directorate, the Engineering and Development Directorate, and the Resident Apollo Spacecraft Program Office - Downey.

4. Deactivation of the command module reaction control system has been formally designated as a HAZARDOUS operation. The Deactivation/Decontamination Manager and his supporting staff will insure that:

(a) The deactivation site is suitable for the operation.

(b) Only required personnel will have access into the deactivation area.

(c) All required equipment is available and is within calibration constraints.

(d) All required personnel are qualified and are trained to perform their assigned functions.

(e) Test discipline is enforced at all times.

(f) All hazardous materials are identified and handled in an approved manner.

11.0 <u>REFERENCES</u>

1. Urbanski, T., Chemistry and Technology of Explosives, Vol. II, Pergamon Press, 1964, p. 473.

APPENDIX

DETAILED DISCUSSION OF CHEMICAL TEST PROGRAM RESULTS

Twelve special tests were conducted to determine the reactions of the chemicals present at the time the incident occurred. A discussion of these special tests is contained in the following paragraphs.

Test 1

Three milliliters of 85-percent nitrogen tetroxide/15-percent water (by volume) were added to 360 milliliters of 25-percent Delchem 2303C/75-percent water (by volume). The quantity of Delchem solution was approximately 6 times the quantity required for neutralization of the 3 milliliters of nitrogen tetroxide solution. The test used an open beaker with the fluids at room temperature (23° C). The nitrogen tetroxide/water solution was slowly added to the Delchem/water solution over a 4-1/2-minute period. The nitrogen tetroxide/water solution was introduced through a burette under the surface of the Delchem/water solution and temperatures were measured with a thermometer.

Upon completion of the nitrogen tetroxide addition, the solution temperature had increased from 23.0° C to 25.0° C. After a total elapsed time of 45-1/2 minutes, the solution temperature had dropped to 24.0° C. At this time, 2 milliliters of 95-percent Freon TF/5-percent nitrogen tetroxide (by volume) were introduced into the solution and observations were continued for an additional 10 minutes. No effect of the Freon TF/nitrogen tetroxide addition was noted and no secondary reactions were observed (none were expected for this case of excess Delchem).

It should be noted that, in the initial neutralization reaction, as nitrogen tetroxide/water is added to the Delchem/water, a rapid exothermic neutralization reaction occurs. Gas is released as the nitrogen tetroxide/water solution is added, but it is volatile nitrogen tetroxide rather than a reaction product. Because of the high volatility of the nitrogen tetroxide/water solution, layering of the Delchem and nitrogen tetroxide solutions did not occur. The bubbling of the nitrogen tetroxide/water solution as it was added provided sufficient agitation to prevent layering.

Test 2

Six milliliters of 85-percent nitrogen tetroxide/15-percent water so-
lution were added to 120 milliliters of 25-percent Delchem/75-percent water.
This quantity of reactants was calculated to provide exact neutralization
without an excess of either reactant. The test setup and procedures were
as described in test 1 except that the nitrogen tetroxide/water solution
was added over a 5-minute period. A vigorous, rapid reaction was observed
with nitrogen tetroxide gas evolution as the nitrogen tetroxide/water was
added, as in test 1.

Upon completion of the nitrogen tetroxide/water additi·   he solution
temperature had increased from 22.5° C to 34.8° C. The so⁙   . cooled
steadily. reaching 26.5° C at an elapsed time of 40 minutes   which time
2 milliliters of 95-percent Freon TF/5-percent nitrogen tetroxide solution
were added. No effect of the Freon TF/nitrogen tetroxide addition was
noted and the solution continued to cool, reaching 25.2° C at an elapsed
time of 60 minutes. No secondary reactions were observed, and none were
expected. No layering was observed. These data are shown in figure A-1.

Test 3

Six milliliters of 85-percent nitrogen tetroxide/15-percent water (by
volume) solution were added to 20 milliliters of 25-percent Delchem/75-
percent water (by volume) solution. These solution concentrations and
relative quantities simulated those present in the Apollo 16 ground sup-
port equipment tank. The test was conducted in an open beaker with the
fluids at room temperature (22° C). The nitrogen tetroxide/water solu-
tion was added to the Delchem/water solution over a 4-minute period using
the same procedures employed in tests 1 and 2.

During the nitrogen tetroxide/water solution addition, the solution
temperature initially increased to 40° C, and then decreased to 38° C as
the excess nitrogen tetroxide/water was added. Large amounts of nitrogen
tetroxide were lost from the beaker during the nitrogen tetroxide/water
addition. On completion of the nitrogen tetroxide/water addition, the
solution had a deep aqua color. Some small amount of secondary reaction
occurred, resulting in slow evolution of gas bubbles. However, the solu-
tion cooled steadily, reaching 24° C after 46 minutes. At that time, 2
milliliters of 95-percent Freon TF/5-percent nitrogen tetroxide (by vol-
ume) were added to the solution with no effect noted. These data are
shown in figure A-2.

In this case, no runaway exothermic secondary reaction occurred,
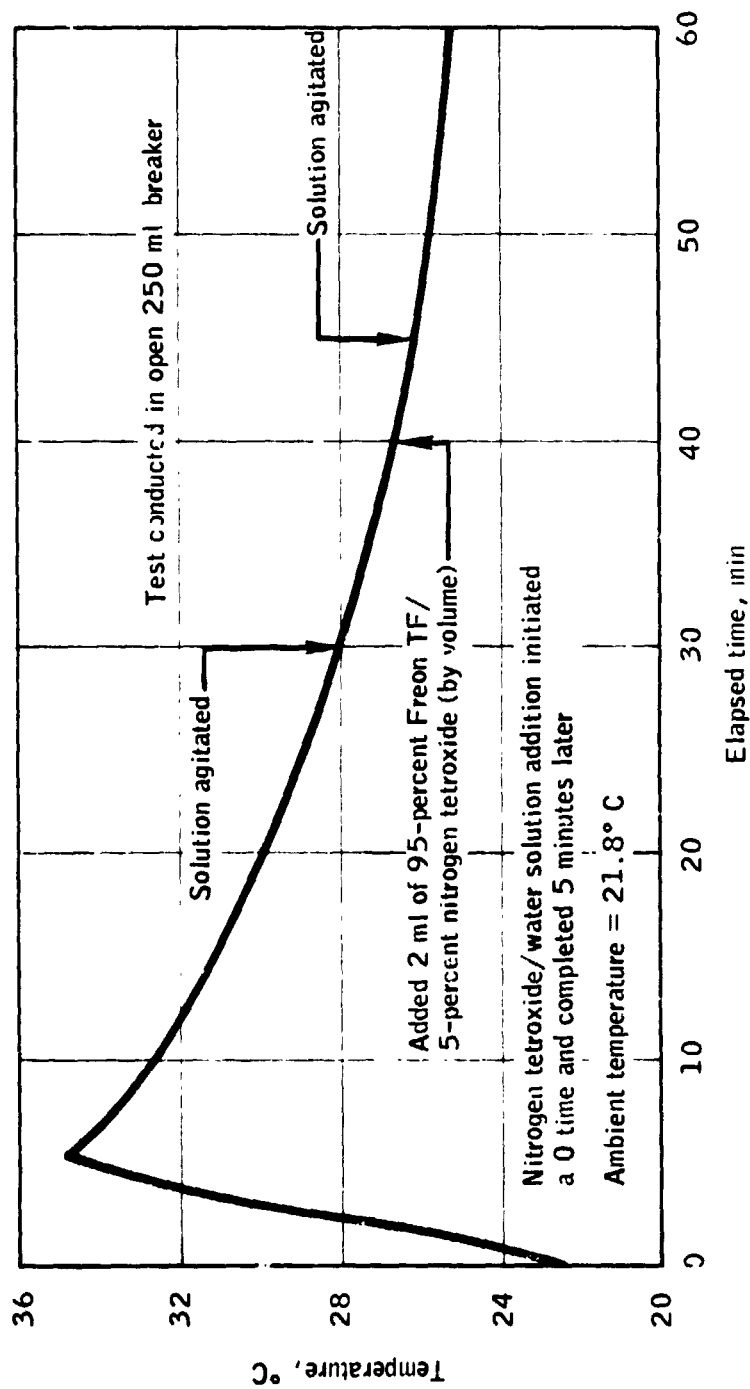although the slow gas evolution indicated that a secondary reaction was

Figure A-1.- Test 2 with solution temperature as a function of time.
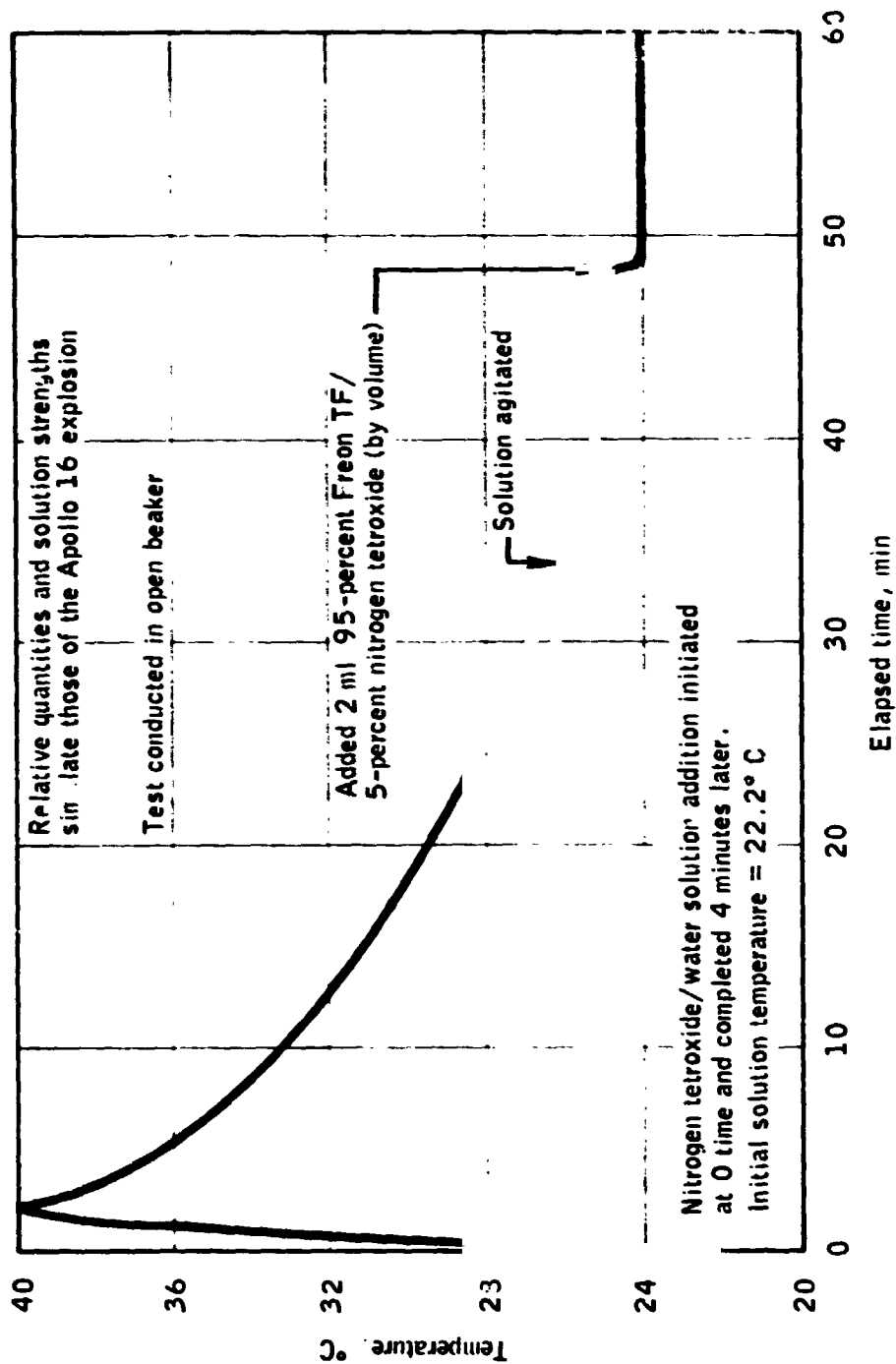
Figure A-2.- Test 3 with solution temperature as a function of time.

proceeding at a slow rate. To investigate the secondary reaction, the solution was warmed slowly on a hot plate. At a temperature of 70 to 75° C, the secondary reaction became very rapid and the solution temperature increased rapidly to 91° C with copious gas evolution. Thus, the secondary reaction was demonstrated.

Test 3 was not believed to have produced the expected runaway exothermic secondary reaction for the following two reasons:

a. Excessive heat loss to the surroundings (i.e., heat was lost to the surroundings faster than it was generated by the secondary reaction, thus preventing a runaway situation).

b. Excess nitrogen tetroxide was lost from the reaction beaker due to its volatility (i.e., perhaps insufficient nitrogen tetroxide remained in solution to promote the secondary reaction at the expected rate).

Test 4

In test 4, solution quantities were doubled to provide an overall larger thermal mass; also, the test was conducted in a 400-milliliter vacuum-jacketed flask to inhibit heat loss to the surroundings and the Delchem/water solution was cooled to 9.5° C in an attempt to inhibit evaporation of the nitrogen tetroxide during the addition of the nitrogen tetroxide/water solution. In this test, 12 milliliters of 85-percent nitrogen tetroxide/15-percent water (by volume) solution were added to 40 milliliter of 25-percent Delchem/75-percent water (by volume) solution. Again, these solution concentrations and relative volumes simulate those of the failure case. The addition took place over a 2-minu.. period. The initial Delchem/water solution temperature was 9.5° C. The peak temperature during the nitrogen tetroxide addition was 32° C and, upon completion of the addition, was 31° C. Again, large quantities of nitrogen tetroxide were lost to evaporation. The final solution was deep aqua in color. The solution initially cooled slightly and then began a slow temperature increase. Slow bubbling and gas evolution were noted. After an elapsed time of 88 minutes, a temperature of 34° C was reached. At this time, an additional 1.5 milliliters of nitrogen tetroxide/water solution were added and this resulted in a 3° C temperature increase and a more rapid rate of temperature rise. At an elapsed time of 102 minutes, an additional 2.5 milliliters of nitrogen tetroxide/water solution were added. The temperature then began climbing rapidly, the secondary reaction gas evolution became vigorous and rapid, and the solution temperature peaked at 98° C and began to fall. A small amount of nitrogen tetroxide/water was again added, but with no effect, indicating completion of the secondary reaction. These data are shown in figure A-3.
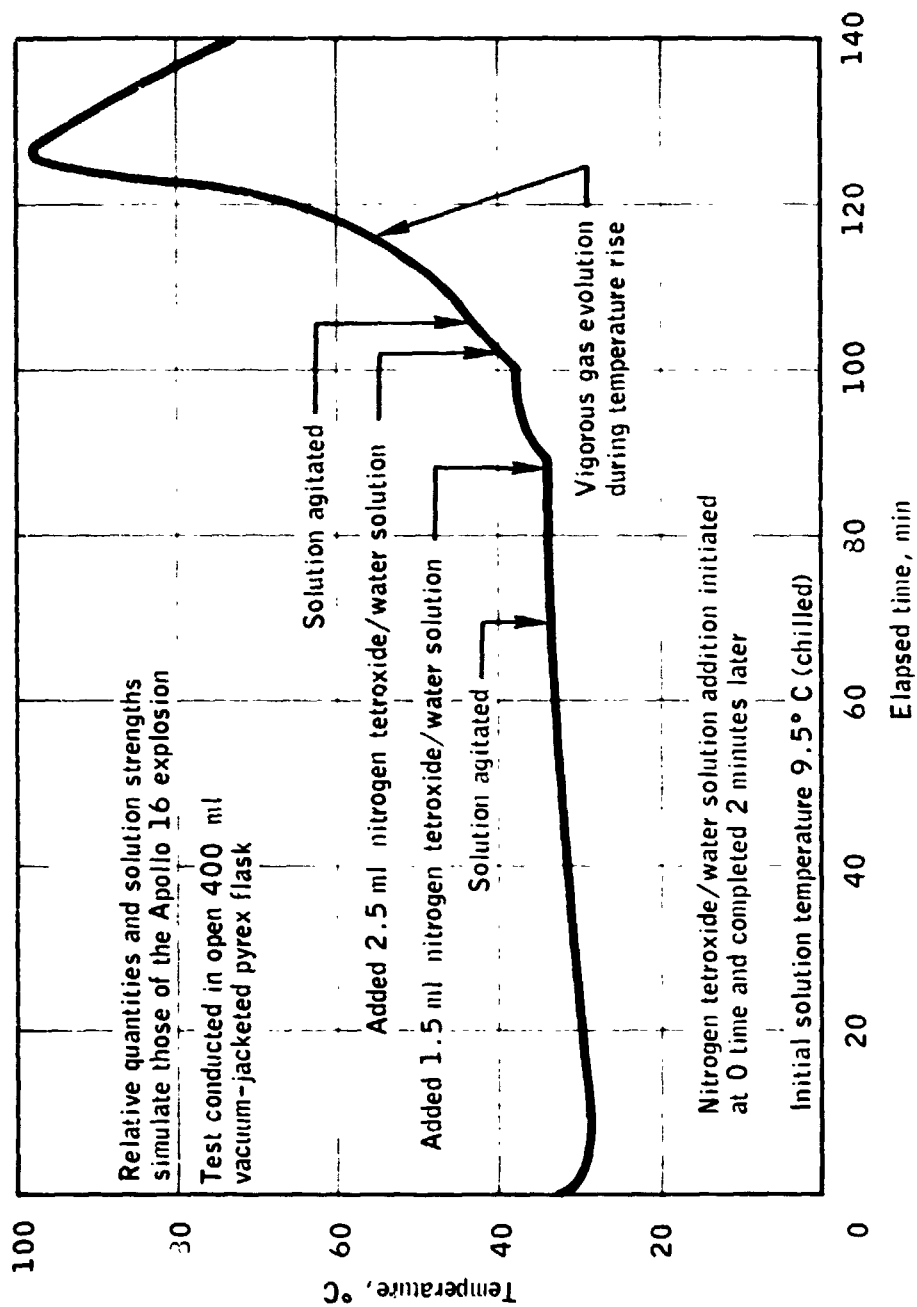
Figure A-3.- Test 4 with solution temperature as a function of time.

Relative quantities and solution strengths
simulate those of the Apollo 16 explosion

Test conducted in open 400 ml
vacuum-jacketed pyrex flask

Solution agitated

Added 2.5 ml nitrogen tetroxide/water solution

Added 1.5 ml nitrogen tetroxide/water solution

Solution agitated

Solution agitated

Vigorous gas evolution
during temperature rise

Nitrogen tetroxide/water solution addition initiated
at 0 time and completed 2 minutes later

Initial solution temperature 9.5° C (chilled)

Temperature, °C

Elapsed time, min

Test 5

A decision was made to alter the solution concentrations while keeping the required amounts of each reactant constant to prevent the loss of nitrogen tetroxide during the addition of the nitrogen tetroxide/water solution, and to avoid chilling the Delchem/water solution (which results in inhibiting the secondary reaction). Thus, to simulate the Apollo 16 incident, a mixture of 10 milliliters of nitrogen tetroxide with 2 milliliters of water and 10 milliliters of Delchem with 30 milliliters of water was required. The solutions, when mixed together, consisted of 10 milliliters of nitrogen tetroxide, 10 milliliters of Delchem, and 32 milliliters water. In order to prepare a less volatile nitrogen tetroxide solution, a 50-percent nitrogen tetroxide/50-percent water solution was made, consisting of 10 milliliters of nitrogen tetroxide and 10 milliliters of water. To keep the total quantities of reactants constant, 10 milliliters of Delchem was mixed with 22 milliliters of water, and the solutions, when mixed together, consisted of 10 milliliters of nitrogen tetroxide, 10 milliliters of Delchem, and 32 milliliters of water - the same as before. In effect, 8 milliliters of water were shifted from the Delchem solution to the nitrogen tetroxide solution to inhibit the nitrogen tetroxide volatility.

In this test, 20 milliliters of 50-percent nitrogen tetroxide/50-percent water (by volume) were added to 32 milliliters of 31-percent Delchem/69-percent water (by volume) over a 6-minute period. The test was performed in the 400-milliliter vacuum-jacketed flask. The nitrogen tetroxide/water solution was added under the surface of the Delchem/water solution. The fluids were initially at room temperature (approximately 18.2° C). The peak temperature reached during the nitrogen tetroxide/water addition was 42° C and the solution temperature dropped to 37.5° C upon completion of the nitrogen tetroxide/water addition. The solution was again a deep aqua color. The solution continued to cool for a short period of time, but then began to heat at an appreciable and accelerating rate. The secondary reaction proceeded vigorously, liberating large quantities of gas. A peak temperature of 101° C was reached after an elapsed time of 18 minutes (12 minutes after completing the nitrogen tetroxide/water addition. Thus, the ability to keep the nitrogen tetroxide in solution appears important to the rate of the secondary reaction. These data are shown in figure A-4.

Test 6

Test 4 was repeated without prechilling the Delchem/water solution in a further attempt to promote the occurrence of the exothermic vigorous secondary reaction. In this test, 12 milliliters of 85-percent nitrogen tetroxide/15-percent water (by volume) solution were added to 40 milliliters of 25-percent Delchem/75-percent water (by volume) solution over a 2.5-minute period. The test was conducted in the same vacuum-jacketed flask
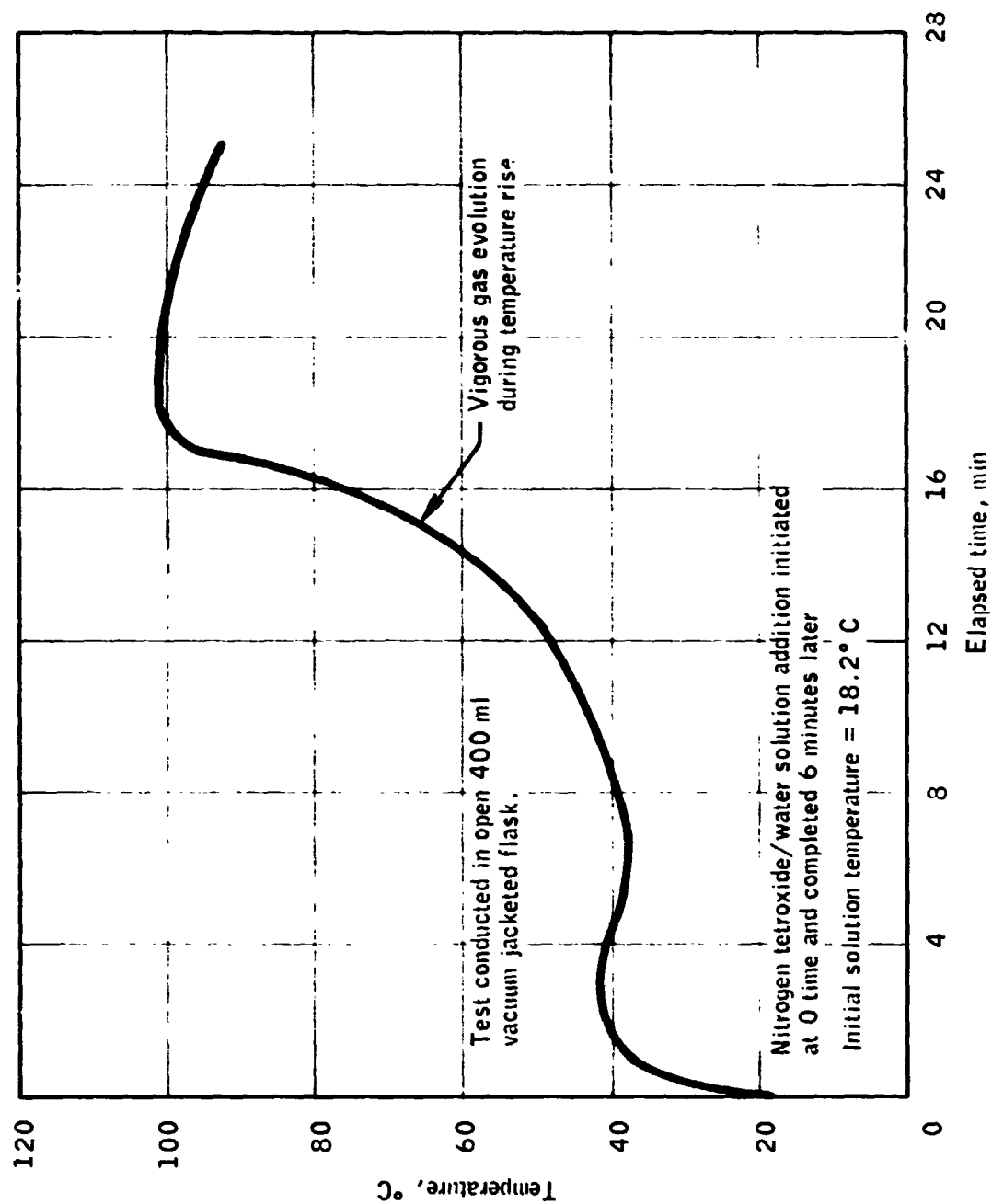
Figure A-4.- Test 5 with solution temperature as a function of time.

Vigorous gas evolution during temperature rise

Test conducted in open 400 ml vacuum jacketed flask.

Nitrogen tetroxide/water solution addition initiated at 0 time and completed 6 minutes later

Initial solution temperature = 18.2° C

with the same procedures used in the previous two tests. The solutions were initially at room temperature (24° C). The peak temperature reached during the nitrogen tetroxide/water addition was 42°C. The resulting solution was again deep aqua in color. The solution cooled slightly and then began a steady heating with secondary reactions indicated by bubbling and gas evolution. The temperature rise rate was slower than in the previous test, with a peak temperature of 87° C reached after an elapsed time of 40 minutes. An additional 1 milliliter of nitrogen tetroxide/water solution was added at an elapsed time of 46 minutes with no effect, indicating that the reaction was complete at this time. These data are shown in figure A-5.

Test 7

A more dilute solution of Delchem was prepared to investigate the importance of the solution temperature, after the neutralization reaction, in promoting the runaway secondary reaction. Thus the 12 milliliters of 85-percent nitrogen tetroxide/15-percent water (by volume) solution were added to 60 milliliters of 16.7-percent Delchem/83.3-percent water (by volume). The Delchem/water solution was prepared by mixing 10 milliliters of Delchem with 50 milliliters of water. Thus the amount of Delchem present was the same as for test 6, but an additional 20 milliliters of water were present to act as an inert dilutent and heat sink. The nitrogen tetroxide/water solution was added over a 5.5-minute period . The test procedure and set-up was the same as in tests 4, 5, and 6. The initial solution temperature was 23.5° C. A peak temperature of 38.5° was reached at the completion of the nitrogen tetroxide/water addition. The resulting solution was deep aqua in color. Substantial nitrogen tetroxide vapors were lost from the flask during the nitrogen tetroxide/water solution addition. Although some gas evolution was noted, indicating a slow secondary reaction, the runaway exothermic secondary reaction did not occur. The solution cooled steadily, reaching 28.5° C at 87 minutes elapsed time. At that time, an additional 2 milliliters of nitrogen tetroxide/water solution were added and this caused a temporary, slight temperature increase but did not promote the runaway secondary reaction.

Test 8

An investigation into the feasibility of using alternate neutralizers for nitrogen tetroxide was made, adding 12 milliliters of 85-percent nitrogen tetroxide/15-percent water (by volume) solution to 200 milliliters of 2-Normal sodium hydroxide solution. This amount of sodium hydroxide is 26 percent in excess of that necessary to neutralize the nitrogen tetroxide.
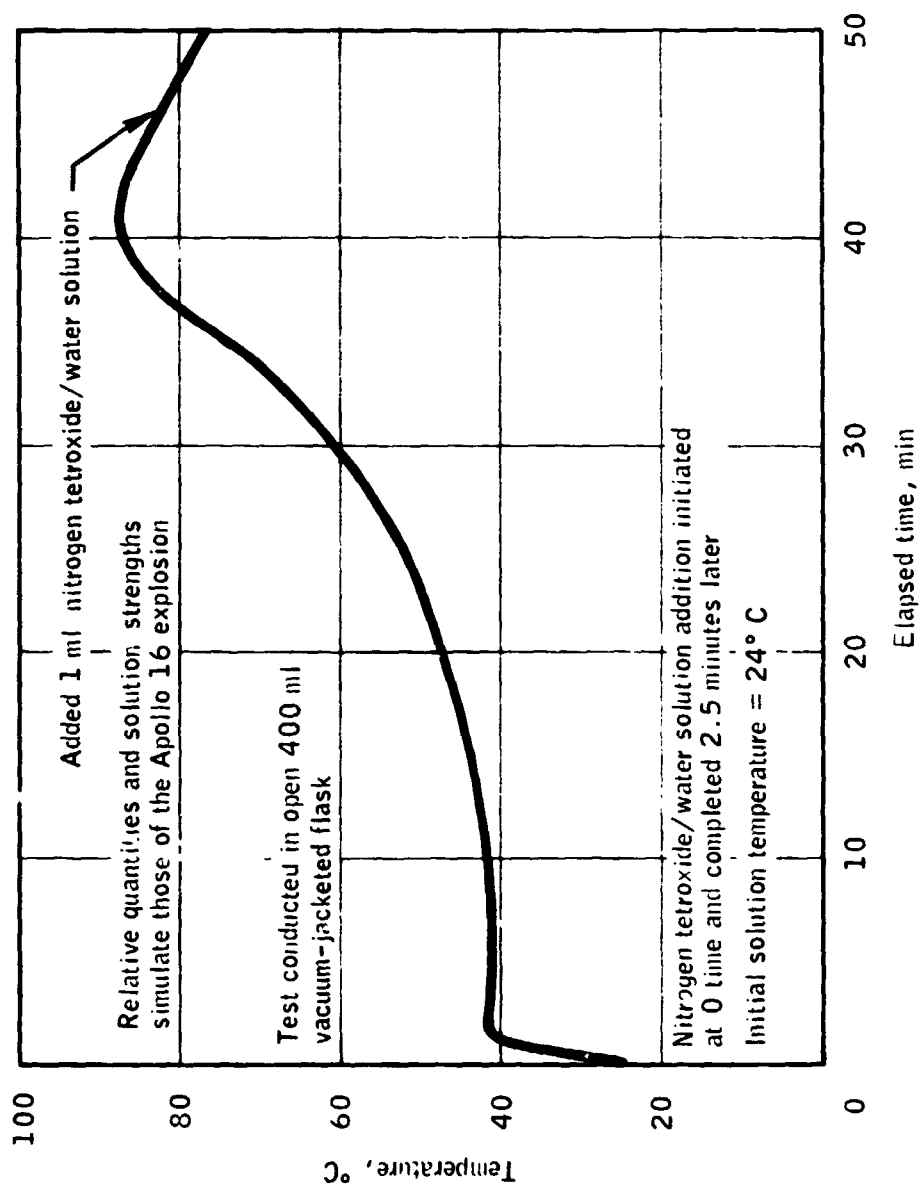
Figure A-5.- Test 6 with solution temperature as a function of time.

The nitrogen tetroxide/water solution was added over a 15-minute period.
The test set-up and procedures were the same as in tests 4 through 7. The
initial temperature of the solution was 27.5° C and the peak temperature
of 42.8° C was reached upon completion of the nitrogen tetroxide/water
addition. The products of neutralization are sodium nitrate and sodium
nitrite in dilute aqueous solution. No gas is evolved from the neutral-
ization reaction. No additional or secondary reactions were observed
over a 2-hour period. These data are shown in figure A-6.

Test 9

Twelve milliliters of 85-percent nitrogen tetroxide/15-percent water
(by volume) were added to 40 milliliters of 25-percent Delchem/75-percent
water (by volume) in a stoppered sidearm Erlenmeyer distillation flask
to measure the volume of gas evolved. The nitrogen tetroxide/water solu-
tion was added with a burette under the surface of the Delchem/water so-
lution over a 12-minute period, and the temperature was measured with a
thermometer. The gas evolved from the reaction was ducted to a water-
filled 5-gallon receiver flask and the evolved gas volume was measured by
water displacement from the receiver flask. System gage pressure was con-
trolled to 1 to 2 inches of water. A small quantity of Dow-Corning 200
silicone oil was floated on the surface of the water in the receiver flask
to prevent water absorption of the evolved gases. The maximum temperature
attained after addition of the nitrogen tetroxide/water solution was 41.0° C
and the solution cooled steadily to room temperature. The resultant solu-
tion was deep aqua in color and slow bubbling indicated some secondary re-
action was occurring, but a runaway, exothermic reaction did not occur.
System leaks prevented measurement of gas evolution.

Test 10

Test 9 was repeated using a stoppered, vacuum-jacketed flask to re-
duce heat losses to the surroundings. The solution quantities and concen-
trations were the same as in test 9. Except for the reaction flask, the
test set-up and procedures were the same as in test 9. The nitrogen tet-
roxide/water addition was made over a 10-minute period. The peak temper-
ature reached was 47.2° C after 99 minutes and, although some moderate re-
action occurred, the vigorous secondary reaction observed in previous tests
did not occur. An additional 1.5 milliliters of nitrogen tetroxide was
added during the test to promote more vigorous reaction, but it was not
effective. The volume of gas evolved from the reaction was 3665 millili-
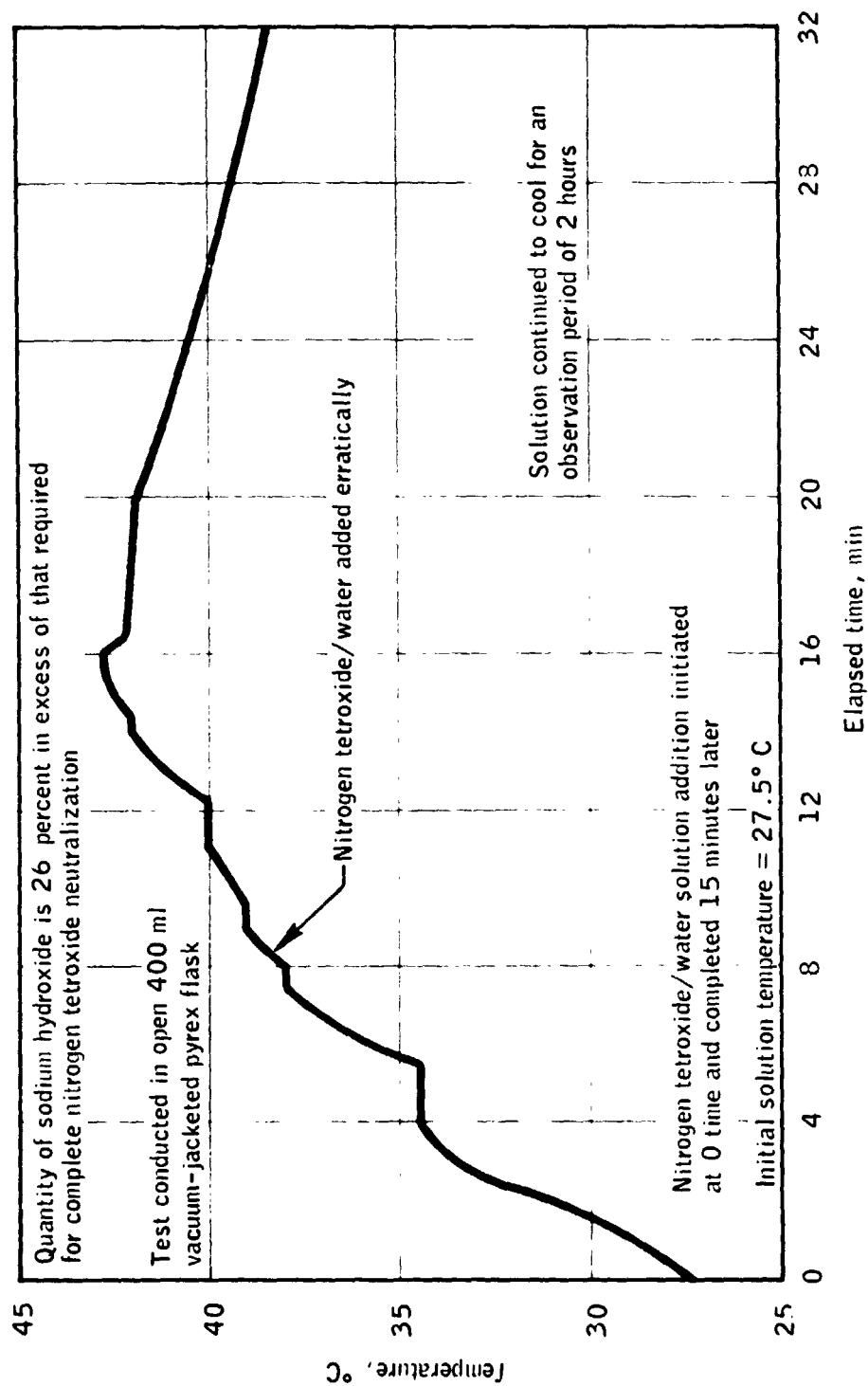ters (measured at 22° C and 1-atmosphere pressure).

Figure A-6.- Test 8 with solution temperature as a function of time.

Test 11

Test 10 was repeated using initially-heated Delchem/water solution
(33.5° C) to attain a higher neutralization temperature and, thus, promote
the vigorous secondary reaction. The peak temperature reached was 54.0° C
after 50 minutes and, again, the vigorous secondary reaction previously ob-
served did not occur. The volume of gas evolved was 2350 milliliters (meas-
ured at 22° C and 1-atmosphere pressure).

Test 12

Test 9 was repeated (i.e., the same solution concentrations, volumes,
Erlenmeyer distillation flask, test set-up, and procedures). Room-temp-
erature solutions were used. In this test, however, the nitrogen tetrox-
ide/water solution was added over a 7-minute period. The solution temper-
ature increased slowly, reaching 96.0° C after 41 minutes. Some heating
was applied to the reaction from a hot plate between 27 minutes and 34.5
minutes, and the vigorous secondary reaction did occur. The volume of
evolved gas (measured at 22° C and 1-atmosphere pressure) was 4770 milli-
liters. No system gas leaks were detected during this test. These data
are shown in figure A-7.

An estimated 15 percent of the nitrogen tetroxide added to the reac-
tion beaker during this test was carried over into the receiver flask and
condensed or absorbed by the Dow-Corning 200 silicone oil (it was deep red
in color). The estimated molecular weight of the evolved gas, based on gas
volume evolved and weight loss from the reactant flask, was 43.7. A non-
quantitative mass-spectrometer analysis of the evolved gases indicated the
presence of NO, NO_2, N_2, N, O, H_2O, C, and H_2. A small amount of an unknown
material of molecular weight 60 was observed. The primary gaseous constitu-
ents, based on mass spectrometer peak height, were NO, NO_2, and N_2, indi-
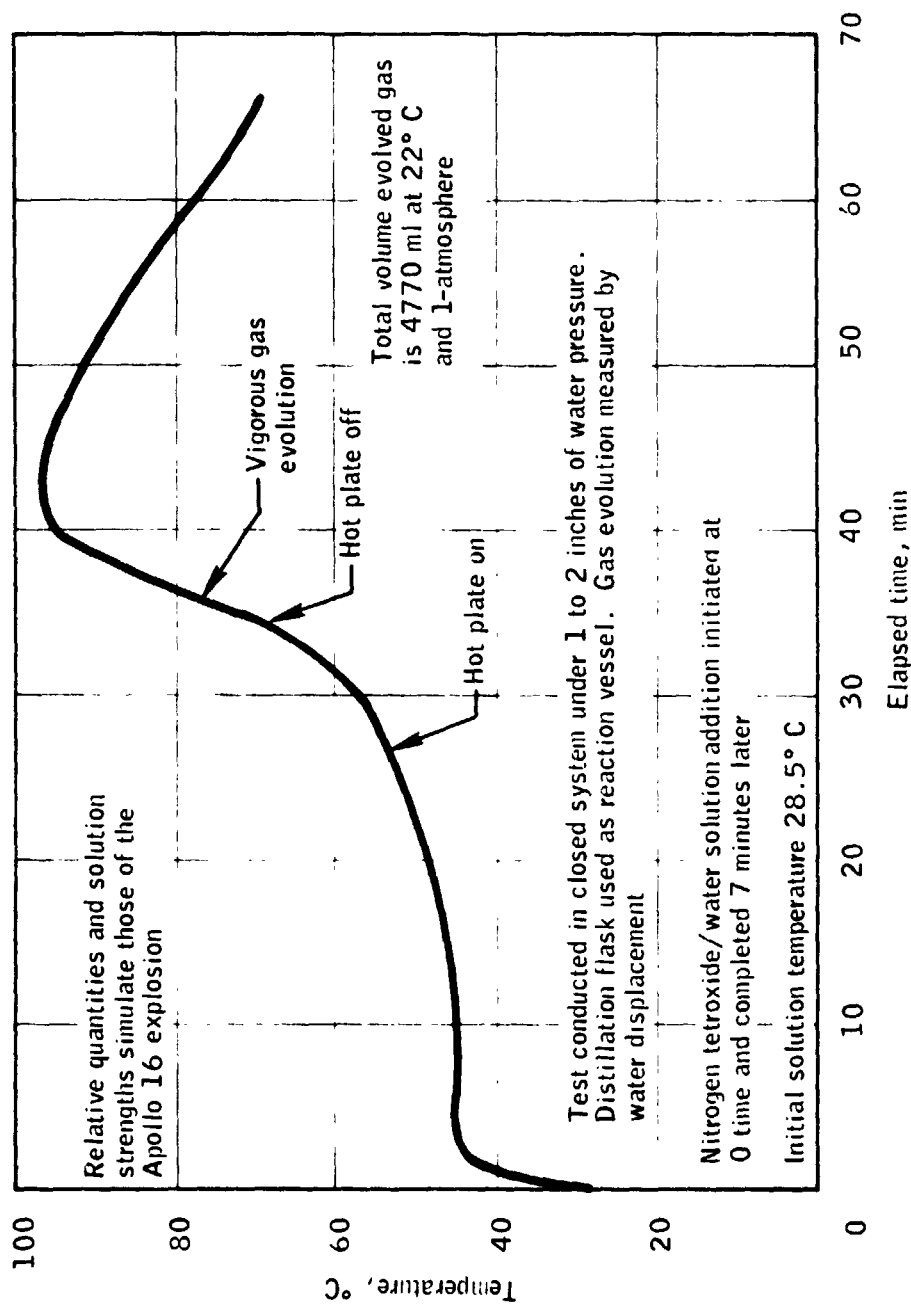cating an average molecular weight probably in the 32 to 36 range.

Figure A-7.- Test 12 with solution temperature as a function of time.